

Phase Diagram in $R_{1-x}A_x\text{MnO}_3$

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Abstract

We study the phase diagram of $R_{1-x}A_x\text{MnO}_3$ ($R=\text{La, Pr, Nd, Sm}$; $A=\text{Ca, Sr, Ba}$) by taking into account the degeneracy of e_g orbitals and the anisotropy of the transfer integral. The electron-electron interaction is treated in the mean field approximation with the optimization of the spin and orbital structures. The global phase diagram is understood in terms of the two interactions, i.e., the super exchange interaction for small x and the double exchange interaction for larger x modified by the orbital degeneracy. The dimensionality of the electronic energy band resulting from the orbital structure is essential to determine the phase diagram. The effects of the Jahn-Teller distortion are also studied.

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The understanding of the rich phase diagram in $R_{1-x}A_x\text{MnO}_3$ ($R=\text{La, Pr, Nd, Sm}$; $A=\text{Ca, Sr, Ba}$) is indispensable for the discussion of its physical properties including the colossal magnetoresistance. These materials have been considered to be the model system of the double exchange mechanism [3–6], i.e., the t_{2g} spins are aligned parallel in order to minimize the kinetic energy of e_g electrons, which are strongly Hund coupled to t_{2g} spins. However this simple picture of the ferromagnetic phase has been questioned recently by several authors [7–14], who stress the importance of the other interactions in addition to the double exchange one. The parent compound LaMnO_3 is an insulator with the A-type antiferromagnetic (AF) ordering and the Jahn-Teller (JT) distortion [15,16], while it should be metallic when only the Hund coupling is considered. Roughly speaking there are two streams of thinking on this issue. One is to regard the JT distortion to be of the primary importance [7,8], which removes the degeneracy of the orbitals. The other is to stress the strong correlation effects of the e_g electrons [11–14]. In this picture the parent material is regarded as a Mott insulator, and the effective Hamiltonian is derived to study the spin and orbital structures [12,13]. In the local density approximation (LDA) and LDA+ U band calculations for $x = 0$ [9], where the effect of the electron correlation is included in a kind of mean field approximation, it is concluded that the JT distortion of the $(3x^2 - r^2)/(3y^2 - r^2)$ -type is important for the A-type spin structure observed experimentally. On the other hand, a recent exact diagonalization study of the effective Hamiltonian [17] suggests that the correlation of the $(3x^2 - r^2)/(3y^2 - r^2)$ -type or $(z^2 - x^2)/(y^2 - z^2)$ -type orbital structure becomes remarkable in the A-type AF phase. As for the doped case ($x \neq 0$), the system becomes ferromagnetic metal for $x > 0.175$ [1,2]. The simple double exchange mechanism [5] is considerably modified as shown below when the anisotropy of the transfer integrals between the e_g orbitals is taken into account. Especially it has been suggested that the orbital degrees of freedom might remain disordered down to low temperatures [14] to explain the anomalous physical properties. Hence the origin of the ferromagnetism should be reexamined taking into account the orbital degeneracy. Near $x = 0.5$ the charge ordering accompanied with the spin and orbital orderings has been observed. With x increased further ($x \cong 0.6$),

the A-type AF structure again appears, which shows quasi-two dimensional metallic behavior [18,19].

In this paper we present an extensive study on the phase diagram of $R_{1-x}A_x\text{MnO}_3$ ($R=\text{La, Pr, Nd, Sm}$; $A=\text{Ca, Sr, Ba}$) in the mean field approximation, which treats both the super and double exchange interactions in a unified fashion at zero temperature. Because the Coulomb interaction is the largest interaction and also the JT distortion disappears for $x > 0.15$ [20], we first study the model with only electron-electron interactions. The spin and orbital structures are optimized, and the global phase diagram is given in the plane of x (the concentration of the holes) and J_s (the super exchange interaction between the t_{2g} spins). The effect of the JT distortion, which turns to be important for $x = 0$, is also studied.

We set up the three-dimensional cubic lattice consisting of the manganese ions. Two kinds of the e_g orbital(γ, γ') are introduced on each site, and the t_{2g} electrons are treated as a localized spin with $S = 3/2$. The Hamiltonian without the JT coupling is given by [12],

$$\begin{aligned}
H = & \sum_{\langle ij \rangle, \sigma, \gamma, \gamma'} \left(t_{ij}^{\gamma\gamma'} d_{i\gamma\sigma}^\dagger d_{j\gamma'\sigma} + h.c. \right) \\
& + U \sum_{i\gamma} n_{i\gamma\uparrow} n_{i\gamma\downarrow} + U' \sum_i n_{ia} n_{ib} + I \sum_{i, \sigma, \sigma'} d_{ia\sigma}^\dagger d_{ib\sigma'}^\dagger d_{ia\sigma'} d_{ib\sigma} \\
& + J_H \sum_i \vec{S}_i \cdot \vec{S}_i^{t_{2g}} + J_s \sum_{\langle ij \rangle} \vec{S}_i^{t_{2g}} \cdot \vec{S}_j^{t_{2g}} . \tag{1}
\end{aligned}$$

$d_{i\gamma\sigma}^\dagger$ is the operator which creates an electron with spin $\sigma(=\uparrow, \downarrow)$ in orbital $\gamma(= a, b)$ at site i , and \vec{S}_i is the spin operator for the e_g electron defined by $\vec{S}_i = \frac{1}{2} \sum_{\sigma\sigma'\gamma} d_{i\sigma\gamma}^\dagger \vec{\sigma}_{\sigma\sigma'} d_{i\sigma'\gamma}$. The electron transfer integral $t_{ij}^{\gamma\gamma'}$, which is estimated by considering the oxygen $2p$ orbitals between the nearest Mn-Mn pair, is represented as $c_{ij}^{\gamma\gamma'} t_0$, where $c_{ij}^{\gamma\gamma'}$ is the numerical factor depending on the orbitals and t_0 is estimated to be $0.72eV$ which we choose the unit of energy below ($t_0 = 1$) [12]. The second line shows the electron-electron interaction terms where U , U' and I is the intra-, inter-orbital Coulomb interactions, and inter-orbital exchange interaction, respectively. This interaction can be rewritten as $-\alpha \sum_i \left(\vec{S}_i(\tau) + \frac{J_H}{2\alpha} \vec{S}_i^{t_{2g}}(\tau) \right)^2 - \beta \sum_i \vec{T}_i(\tau)^2$ [14]. Here the spin operator \vec{S}_i and the iso-spin operator $\vec{T}_i = \frac{1}{2} \sum_{\gamma\gamma'\sigma} d_{i\sigma\gamma}^\dagger \vec{\sigma}_{\gamma\gamma'} d_{i\sigma\gamma'}$

for the orbital degrees of freedom are introduced, and the two positive coefficients α and β , which are defined by $\alpha = 2U/3 + U'/3 - I/6$ and $\beta = U' - I/2$, represent the interaction to induce the spin and iso-spin moments, respectively. The last line is the sum of the Hund coupling and the AF interaction between the nearest neighboring t_{2g} spins. Here we adopt the mean field approximation by introducing the order parameters $\langle \vec{S}_i \rangle$, $\langle \vec{S}_i^{t_{2g}} \rangle$, and $\langle \vec{T}_i \rangle$. These order parameters are determined to optimize the mean field energy at zero temperature. For both spin and orbital, the four types of the ordering are considered, that is, the ferromagnetic (F-type) ordering, where the order parameters are uniform, and the three AF-like orderings, i.e., the layer-type (A-type), the rod-type (C-type) and the NaCl-type (G-type) AF orderings. Hereafter, types of the orderings are termed as, for example, (spin:C), and so on.

In Fig. 1, the spin and orbital phase diagram is shown for the set of parameters $\alpha = 70 \gg \beta = 2.5$. In this rather extreme case the regions dominated by the super exchange and double exchange interactions are separated, and it is easy to obtain the physical picture. $\alpha/\beta \gg 1$ corresponds to the situation where $1/(U' - I) \gg 1/U, 1/(U' + I)$. In Fig. 1, the spin structure changes as $F \rightarrow A \rightarrow C \rightarrow G$, as J_s increases, which is consistent with the exact diagonalization study [17]. We begin with the discussion of the parent material ($x = 0$) where only the super exchange interaction is effective. For spin:A, which is observed in LaMnO_3 , the most stable orbital structure is the orbital:G $([3z^2 - r^2] + [x^2 - y^2])/([3z^2 - r^2] - [x^2 - y^2])$ as shown in Fig. 1. When the ratio α/β is changed, the orbital changes continuously from orbital:G $([3z^2 - r^2] + [x^2 - y^2])/([3z^2 - r^2] - [x^2 - y^2])$ for $\alpha/\beta \gg 1$ to orbital:G $(y^2 - z^2)/(z^2 - x^2)$ for $\alpha/\beta \sim 1$, and to $(3z^2 - r^2)$ for $\alpha/\beta = 0$. For the actual compound, we expect $\alpha \gtrsim \beta$ and orbital:G $(y^2 - z^2)/(z^2 - x^2)$ is the most stable. The experimentally observed orbital:G $(3x^2 - r^2)/(3y^2 - r^2)$ is never the most stable solution, which can be understood as follows. There are three possibilities for the intermediate states of the super exchange processes, i.e., the occupancy of the two orbitals (a) with the parallel spins (the energy $U' - I$) or (b) antiparallel spins ($U' + I$), and (c) the double occupancies of the same orbital (U) [12,13,21,22]. Then the relative importance of the states (a) compared with (b)

and (c) is changed when α/β is changed. Let us compare the energy gains due to the super exchange processes in orbital:G $(y^2 - z^2)/(z^2 - x^2)$ and orbital:G $(3x^2 - r^2)/(3y^2 - r^2)$. For the processes using states (a) and (b), the magnitudes of the transfer integrals and hence the energy gain are the same, while for the process using (c), the energy gain is always larger for $(y^2 - z^2)/(z^2 - x^2)$ compared with $(3x^2 - r^2)/(3y^2 - r^2)$. Then there is no chance for $(3x^2 - r^2)/(3y^2 - r^2)$ to be the most stable structure for any value of α/β . Hence the JT coupling is important in addition to the electron-electron interactions at $x = 0$. We introduce the JT distortion observed experimentally and its coupling to the e_g electrons. We consider the two shorter Mn-O bonds and the one longer bond in the MnO_6 octahedron, and its bond length is represented as $d_{long} = d_0(1 + 0.056)$ and $d_{short} = d_0(1 - 0.028)$, respectively, as we follow the structural data [15]. The change of the transfer integrals is estimated in terms of the dependence of the $3d - 2p$ hopping t_{pd} on the distance d as $t_{pd} \propto d^{-7/2}$ [23]. We vary the splitting of the energies (g) between the two orbitals as the parameter and found

[1] The wave functions are saturated to become $(3x^2 - r^2)/(3y^2 - r^2)$ when g is about the half of the transfer energy t_0 . This value is much smaller than what is expected in the absence of the electron-electron interactions. The magnitude of the isospin moment $|\vec{T}_i|$ is already induced almost fully in terms of the strong electron-electron interactions, and the role of the JT coupling is to fix the direction of \vec{T}_i . [2] The spin:A is stabilized relative to spin:F by JT distortion. The phase boundary $J_s(FA)$ between A and F is shifted from $J_s(FA) = 0.014$ for $g = 0$ to $J_s = 0.007$ for $g = 1.0$. This tendency is in agreement with the other calculations [9,10], but the physics is different. In the band calculation, the ground state without the JT distortion is the ferromagnetic metal and the enhanced AF exchange between layers is due to the reduced double exchange interaction by JT distortion [9]. In our calculation, on the other hand, only the super exchange interactions are relevant because the large gap has been already opened up due to the strong electron-electron interactions. The stabilization of the A-AF is clearly understood in terms of the change of the super exchange interaction by the orbital rearrangement.

Now let us turn to the doped case ($x \neq 0$). The orbital structure in spin:F is quite

sensitive to the carrier concentration, that is, it changes continuously as x increases from orbital:G($x^2 - y^2$)/($3z^2 - r^2$) near $x = 0$ to ($x^2 - y^2$) for $x \cong 0.3$, and to orbital:A($[3z^2 - r^2] + [x^2 - y^2]$)/($[3z^2 - r^2] - [x^2 - y^2]$) for $0.3 < x < 0.8$ and finally ($3z^2 - r^2$) for $x = 0.8$, as shown in Fig.1. On the other hand the orbital in spin:A and spin:C almost remains ($x^2 - y^2$) and ($3z^2 - r^2$), respectively, except for $x = 0$, in contrast to spin:F case. The phase boundary $J_s(FA)$ increases linearly near $x = 0$, and turns to decrease to have a minimum $J_s(FA) \cong 0$ at around $x = 0.3$, where both spin:F and A have the ($x^2 - y^2$) orbital. The linear increase is due to the difference in the location of the band edges for spin:F and spin:A structures. This feature remains true even when the canting in the spin:A is taken into account because it gives the energy gain only of the order of $\sim x^2$ [5]. The minimum of $J_s(FA)$ around $x \cong 0.3$, separates rather clearly the two regions dominated by the super exchange ($x \lesssim 0.3$) and the double exchange interactions ($x \gtrsim 0.3$). In the doped case the shape of the density of states and the Fermi energy is crucial to determine the double exchange energy, which depends on both spin and orbital structures. Especially The dimensionality and the van-Hove singularities of the density of states depends strongly on the orbital structure. Therefore, in that sense, the double exchange mechanism is considerably modified from the conventional one, when the anisotropy of the transfer integrals and the electron-electron interaction are taken into account. In the region of $x < 0.3$, the orbital:G($x^2 - y^2$)/($3z^2 - r^2$)- and orbital:F($x^2 - y^2$)-type structures realized in the spin:F and spin:A phases respectively, and the band becomes two-dimensional. Here, the density of states has a logarithmic singularity at $\varepsilon = 0$ and decreases monotonously as $|\varepsilon|$ with the steps at $\varepsilon = \pm 3t_0$. In the low carrier concentration region, the above type of the density of states is more favorable than the three dimensional one due to the step at the band edge. In this case there is no difference in the kinetic energy of the carriers between spin:F and spin:A, and J_s favors spin:A. Then the F region in Fig. 1 for $x < 0.3$ is stabilized by the super exchange interaction. In the region of $x > 0.3$, the orbital structure is rearranged as orbital:A($[3z^2 - r^2] + [x^2 - y^2]$)/($[3z^2 - r^2] - [x^2 - y^2]$)-type, where the band structure is essentially three dimensional, but the density of states has two peaks at

$\varepsilon \cong \pm 2t_0$ and resembles that of the one-dimensional band. Eventually the $(3z^2 - r^2)$ orbital appears at $x = 0.8$ and gives the one dimensional-like band along the z -axis where the density of states has the peak structures at $\varepsilon = \pm 3t_0$. Then the adjusting of the orbital structure with increasing x occurs in order to minimize the kinetic energy, i.e., the center of mass for the occupied states. When one consider the occupied orbital, the energy position of the band edge does not depend on the dimensionality of the dispersion. Then only the shape of the density of states matters, and one dimensional-like dispersion is advantageous in this viewpoint. For spin:C, the orbital is $(3z^2 - r^2)$ almost always except at very small x . This can be easily understood because the spin structure allows the electron motion only along the z -axis. For spin:G, the electron motion is blocked in all directions and the double exchange energy gain is absent. Then the electronic energy does not depend on the orbital structure in the limit of strong electron-electron interaction.

In Fig. 2, we present the calculated phase diagram in the case of $\alpha = 8.1$, $\beta = 2.5$, which is more relevant to the actual manganese oxides. This set of parameters is complementary to that in Fig. 1 because both α/β and α are smaller. In comparison with the results in Fig. 1, the spin:F region dominated by the super exchange interaction, is extended to the region with larger x . This results in the merging of the super exchange and double exchange regions. First consider the spin:F state. At $x = 0.0$, the orbital structure in the spin:F phase is the same as that in Fig. 1. What is different from Fig. 1 is that as x is increased the orbital becomes orbital:C $([3z^2 - r^2] + [x^2 - y^2])/([3z^2 - r^2] - [x^2 - y^2])$ -like structure instead of $(x^2 - y^2)$ and to the orbital:A $([3z^2 - r^2] + [x^2 - y^2])/([3z^2 - r^2] - [x^2 - y^2])$ around $x = 0.6$. The two dimensional $(x^2 - y^2)$ -like structure appears for $x \cong 0.9$ where the mixing of the two bands is important.

As for the spin:A, C, G, the orbital remains basically the same as in Fig. 1. Then it is concluded that the orbital structure is sensitive to the interactions only in spin:F. This is related to the the degeneracy of the orbital structures [14]. Actually all the obtained orbital structures in Figs. 1 and 2 belong to the lowest degenerate states discussed in [14].

We now discuss the comparison between the mean field phase diagram in Fig. 2 and

the experiments. In the present mean field calculation, the ferromagnetic phase, i.e. the spin:F phase is growing up with increasing x from the insulating state, and it becomes most remarkable around $x = 0.3$, as shown in Fig. 2. The global feature of the spin:F phase is quite consistent with the experimental results in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, where the ferromagnetic phase appears at about $x = 0.08$ and it survives up to $x = 0.5$. It is worth to note that, however, the origin of the ferromagnetic phase is far from the conventional double exchange mechanism, i.e., both the super exchange and the double exchange interactions modified by the orbitals are relevant in the region $0.2 < x < 0.4$. The orbital ordering in spin:F, if observed experimentally by neutron and/or X-ray diffraction, will give important clues to the interactions because it depends sensitively on the parameters as described above. The another possibility is the orbital fluctuation is so large that the orbital liquid state is realized [14]. The RPA analysis of the mean field solutions is left for the future work.

The another implication to the experimental results is about spin:A phase appearing around $x > 0.5$. In $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$, the ferromagnetic metallic phase is realized up to about $x = 0.48$ and the CE-type AF structure with the charge ordering tunes up [18,19]. With further increasing of x , the metallic state with spin:A again appears at about $x=0.53$, and the large anisotropy in the electrical resistivity is observed in this phase. The similar metallic phase accompanied with spin:A is also reported in $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ [19]. Although the charge ordered phase is not considered, i.e., the long range Coulomb interaction is neglected, in the present work, the global phase change, as spin:A insulator ($x \sim 0$) \rightarrow spin:F metal ($0.1 \lesssim x \lesssim 0.5$) \rightarrow spin:A metal ($0.55 \lesssim x$), is well reproduced when we fix J_s to be around 0.02eV , which is a reasonable value, as shown by the broken line in Fig. 2. It is predicted that the $(x^2 - y^2)$ -type orbital structure should be realized in this spin:A metallic phase, in contrast to the insulating phase with spin:A appearing at $x = 0.0$. Furthermore, the AF interaction between layers is expected to be enhanced in comparison with that at $x = 0.0$, because the ferromagnetic interactions originated from the both double exchange and super exchange interactions are prohibited in this direction. By the same reason it is predicted that the spin canting does not occur in this spin:A metal as observed in [19], in contrast to

the spin:A in the small x region which has been discussed by de Gennes [5]

In summary we have studied the phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ in the plane of x (hole concentration) and J_s (AF exchange interaction between the t_{2g} spins) in the mean field approximation. The global features can be understood in terms of the interplay between the super exchange and the double exchange interactions which are considerably modified with taking the orbital degrees of freedom into account. The dimensionality of the energy band attributed to the orbital structure plays essential roles to determine the phase diagram. The orbital structure is sensitive to changes of the carrier concentration and the interactions only in the ferromagnetic state, which suggests the importance of the ordering/disordering of the orbital on the origin of the ferromagnetism in the perovskite manganites.

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Figure captions

Figure 1. The mean field phase diagram in the plane of the carrier concentration (x) and the antiferromagnetic interaction J_s between the t_{2g} spins. The strength of the interactions are set as $\alpha = 70 \gg \beta = 2.5$. The schematic orbital structure in the each phase is also shown.

Figure 2. The calculated mean field phase diagram with $\alpha = 8.1$ and $\beta = 2.5$ case.